2015 DOE Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Arlington, VA

A Novel Lubricant Formulation Strategy for 2% Fuel Efficiency Improvement

Project ID: FT024

Northwestern University and Argonne National Laboratory

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June 11, 2015

Overview

Timeline

- Project start date: Jan. 18th, 2014
- Project end date: Sep. 30th, 2016
- Percent complete: 40-45 %

Budget

- Total project funding
  - DOE share: $ 1,000,000
  - Contractor share: N/A
- Funding received in FY14: $444,444
- Funding for FY15: $ 277,777

Goals/Barriers Addressed

- 2% fuel efficiency requires 30-40 % boundary friction reduction plus other means of friction control.
- Friction should be reduced in the entire lubrication range with high thermal stability.
- Energy efficient additives should not have adverse interaction with existing necessary additives.

Partners

- Northwestern University — Lead
- Argonne National Laboratory

In collaboration with

- Ashland, Inc.
- General Motors

Relevance and Objectives

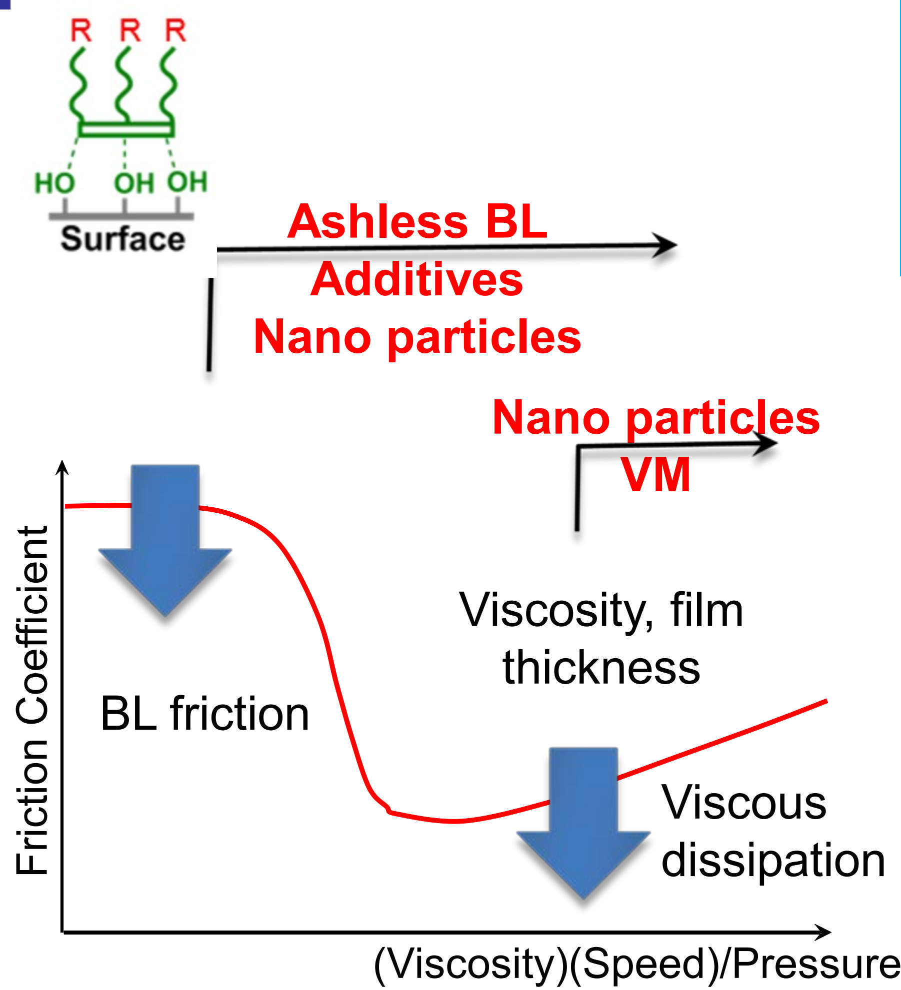
- **Targets**: **Novel energy efficient Friction modifiers (FMs), viscosity modifiers (VMs), Nano Particles (NPs)**.

- **Overall Objective**: Novel lubricant formulations for improving vehicle fuel efficiency by at least 2 % without adversely impacting vehicle performance or durability.
  - Reducing friction due to asperity rubbing in start-up and low-speed;
  - Temporarily reducing the lubricant viscosity (temporary shear-thinning) in medium- to high-speed cruise operations;
  - Suppressing oil aeration or foaming responsible for lubrication breakdown in high-speed operations.

- **FY 14 Objectives** (January 2014 through March 2015)
  - Synthesize thermally stable S-and-P-free heterocyclic additives for BL improvement;
  - Functionalize solid-state-lubricating nanoparticles for friction reduction and scuffing prevention;
  - Design and synthesize a novel di-block copolymer-based VM;
  - Conduct tribological studies and confirm at least 10%% boundary lubrication friction reduction together with significant wear reduction.

Strategy and Approaches

Key ingredients: FMs, VMs, NPs.



- ❑ Ashless BL Additive design and synthesis
- ❑ Additive selection via nano-friction tests:
- ❑ Additive evaluation via pin-on-disc tests

- ❑ Nanoparticle friction

- ❑ VM design and synthesis
- ❑ VM selection via viscosity-T, S tests
- ❑ VM evaluation via film thickness measurements

Modeling

Milestones

Milestone	Status
1. Initial Heterocycle-Based Additive Design and Synthesis Go/No-go Decision: at least 10% boundary friction reduction	Completion
2. Temporary Thinning Modifier, Design and Synthesis of Initial Compositions Go/No-go Decision: demonstration of temporary shear thinning	On Track
3. Nanoparticles in Lubricants and Characterization Go/No-go Decision: no severe wear	Completion
4. Model-Assisted Optimal Molecular and Mixing Design: Basic model Development	Completion
5. Initial Investigations of Surface Functionalization and Additive-Surface Interactions	Complete
6. Rheological Properties of Initial Lubricant Formulations: with New Additives	On Track
7. Friction and Wear Tests on Initial Formulations: Laboratory Steady State Tests of Initial Modified Fluids	Complete

Technical Accomplishments and Progress

Novel Boundary Lubrication Friction Modifiers

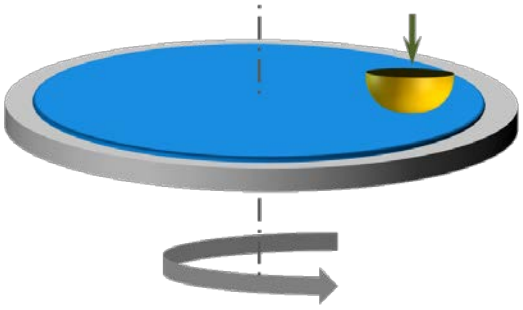
Novel Friction Modifiers Made

- Heterocycles 1 (TbenzylT, TC12T, TC18T, TC12C18T ...) ,
- Heterocycles 2 (C12Cyc and C18Cyc)
- Heterocycles 3 (C6triaz, C12triaz, 4C6Ptriaz, and 4C12Ptriaz)

Tested In Group II, III, and IV oils

- *Disk: E52100 alloy steel*
- Pin: M50 steel ball (Ø 9.53 mm)
- Linear speed: **1.5 mm/s — 150 mm/s**
- Applied load: **3 N** or **15.6N**
- Temperature: **25 °C — 200 °C**

R: Alkyl chains (C6, C12, or C18), benzyl, phenethyl, cyclohexyl, or their hybrids.

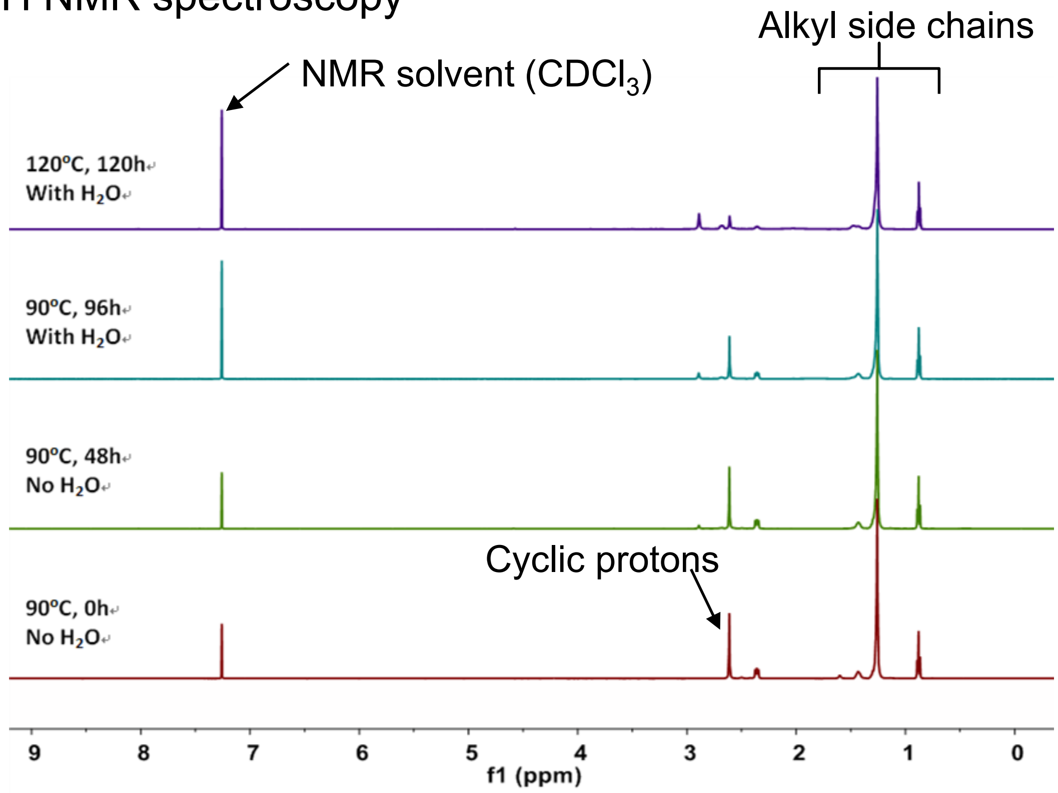


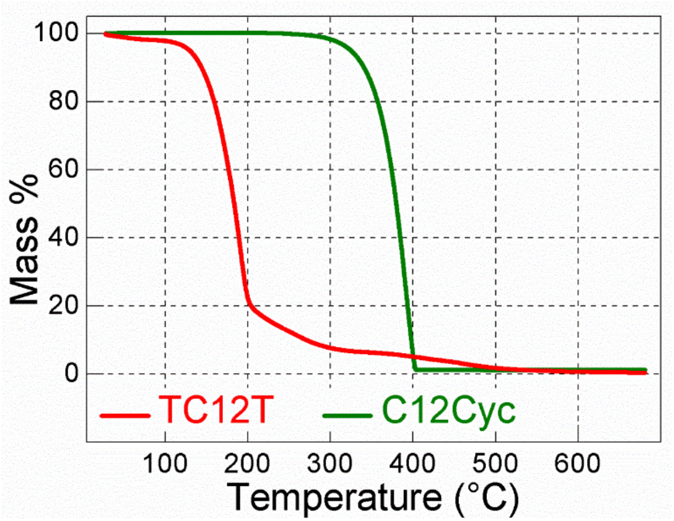
Technical Accomplishments and Progress

Novel Boundary Lubrication Friction Modifiers: thermal stability

Strategy to enhance the thermo-stability:
- — Spacers (**heterocycle 2**)
- — Aromatization (**heterocycle 3**)

^{1}H NMR spectroscopy





TGA analyses demonstrates improved thermo-stability as well.

^{1}H NMR spectra for C12Cyc during extended heating are shown here only. No structural changes. The other heterocycles 2 and 3 have the same thermal stability.

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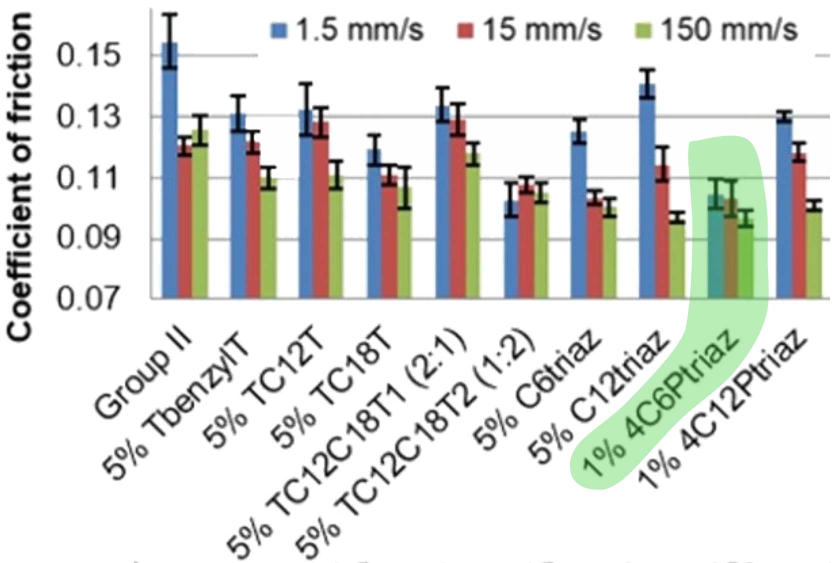
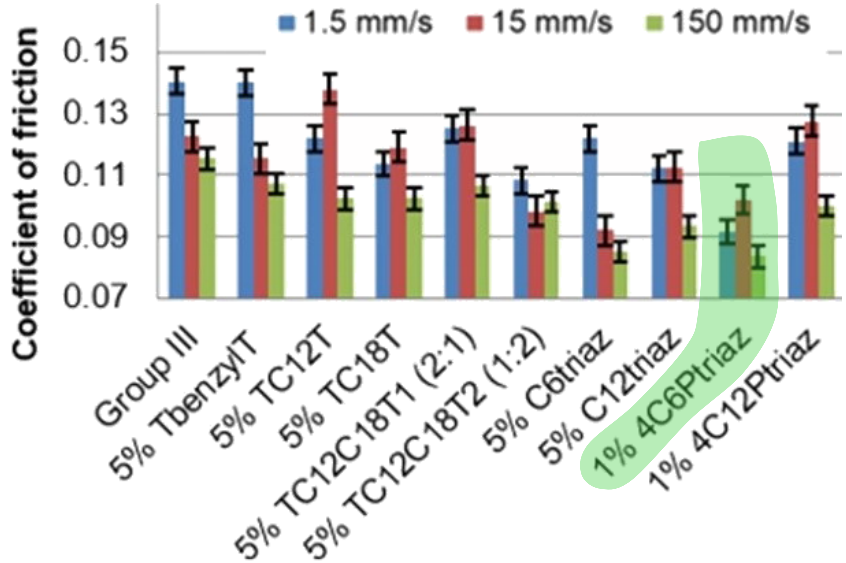
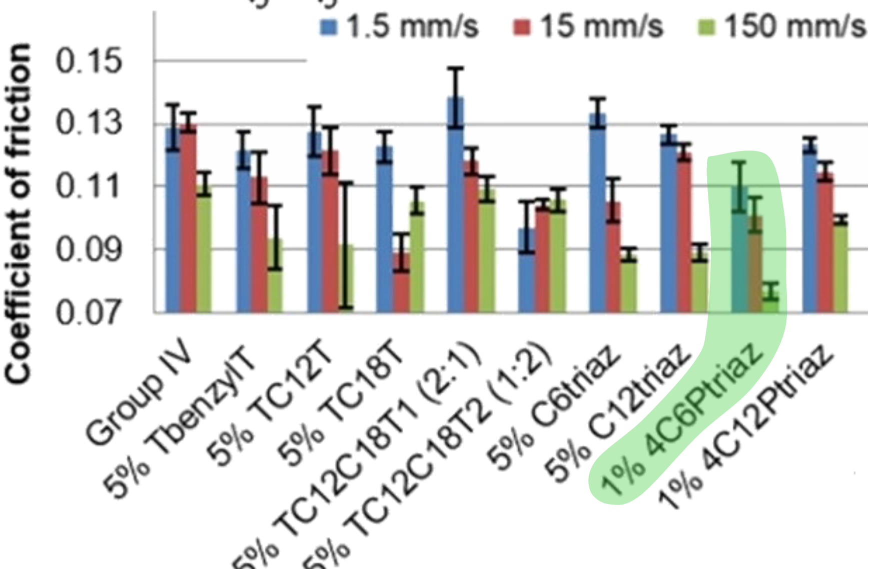
Technical Accomplishments and Progress

Novel Boundary Lubrication Friction Modifiers: Friction







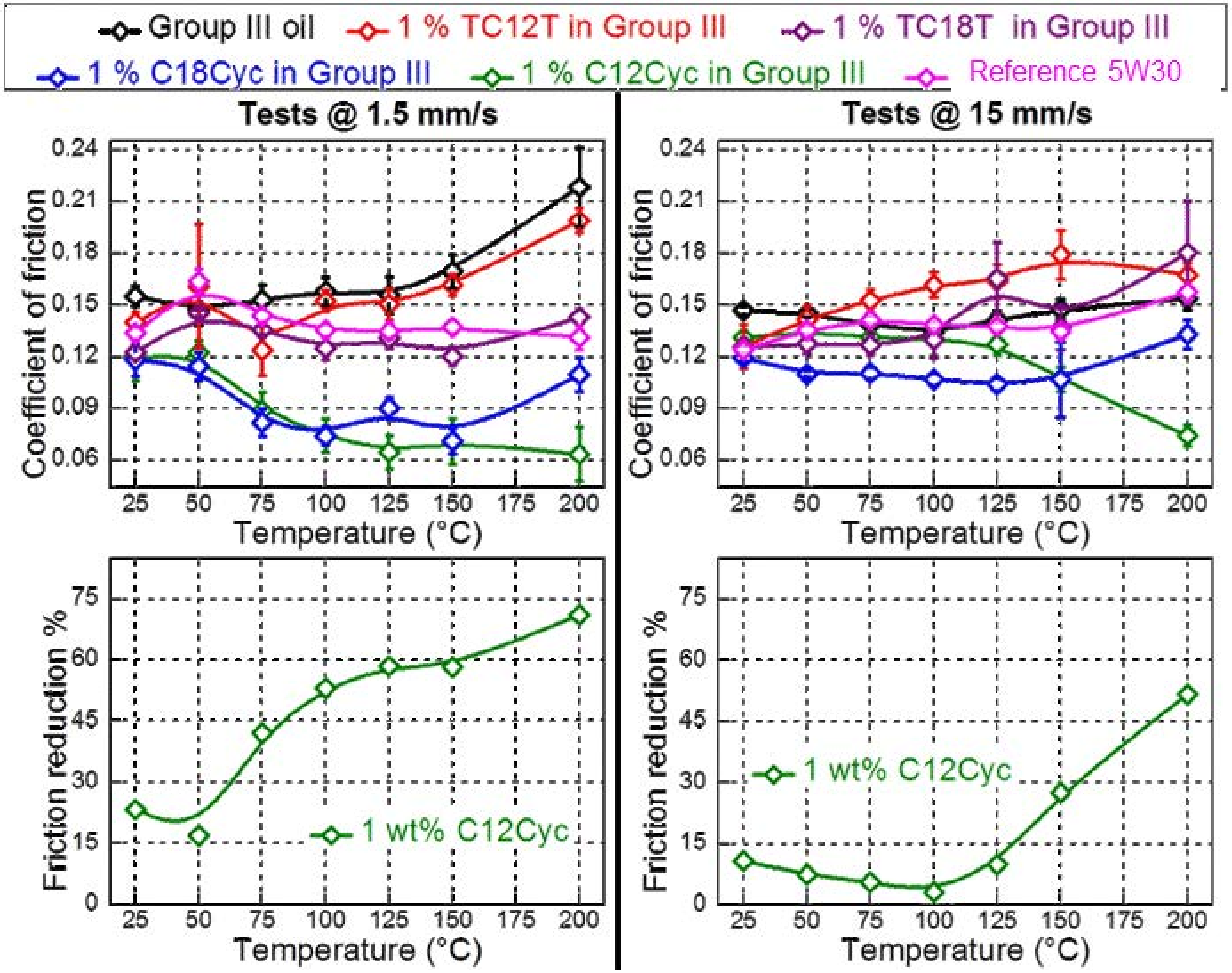
Heterocycles 3

4C6Ptriaz — an excellent BL additive at room temperature!

Only 1 wt% 4C6Ptriaz is able to reduce friction by ~ **25 %** to ~ **40 %** at different speeds.

Technical Accomplishments and Progress

Novel Boundary Lubrication Friction Modifiers: Friction



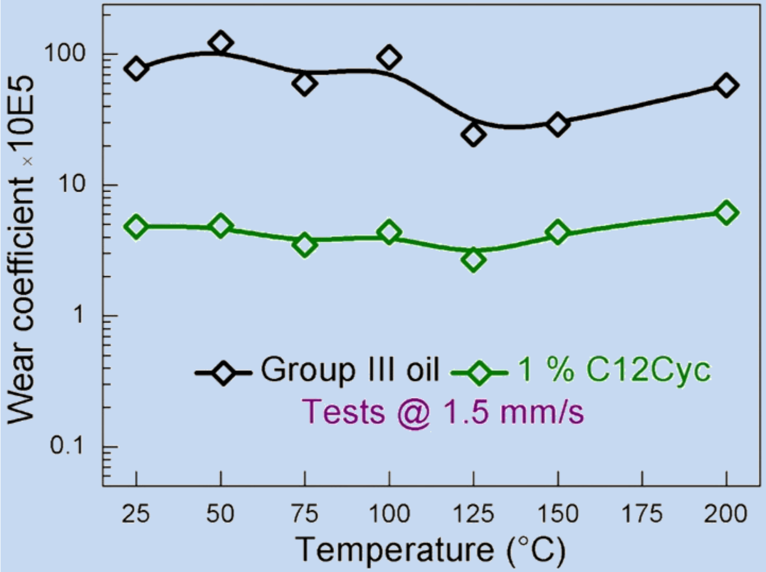
Heterocycles 2
Percentage of friction reduction at **1.5 mm/s** is all well above **40 %** (> 75 ºC) and reaches a value more than **70 %** at 200 ºC!

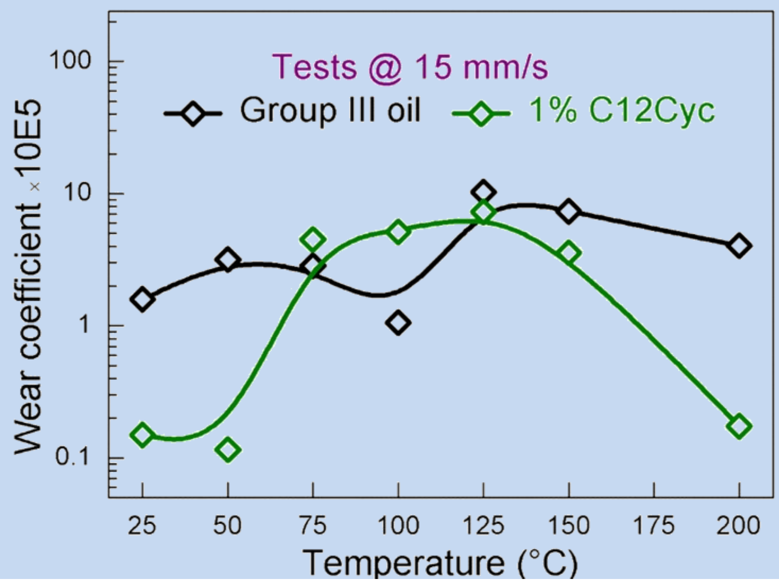
As temperature changes from 25 ºC to 200 ºC at **15 mm/s**, the percentage increases from ~ 15 % to ~ **50 %**!

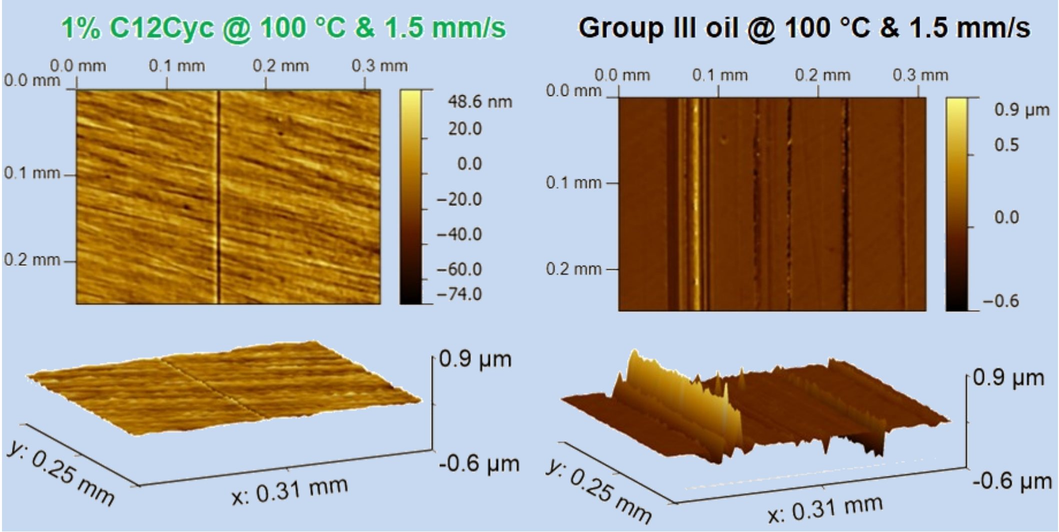
The base oil with the heterocycle 2 additive has a significantly lower CoF than fully formulated motor oil in the BL regime!

Technical Accomplishments and Progress

Novel Boundary Lubrication Friction Modifiers: Wear







Heterocycles 2
Wear is also greatly eliminated by using **C12Cyc**.

The novel BL additive is capable of reducing wear coefficients by more than **one order of magnitude**!

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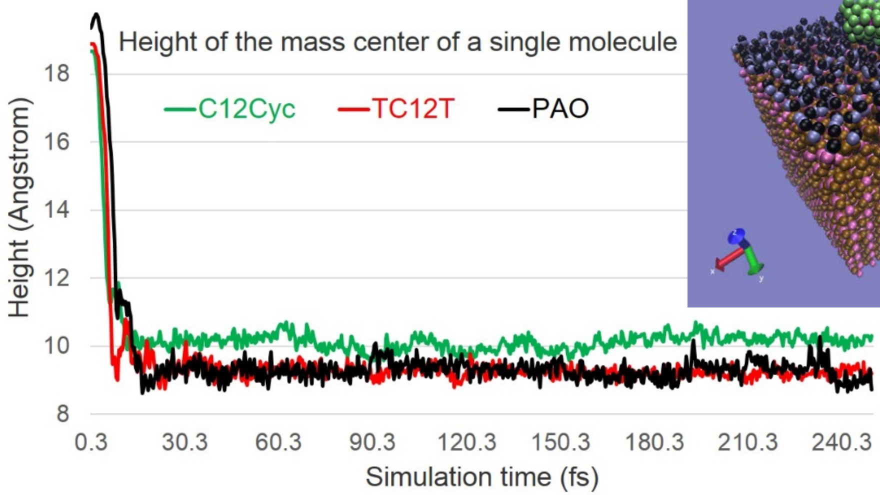
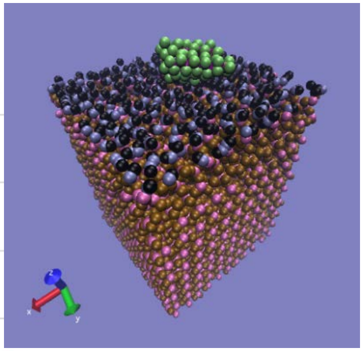
Technical Accomplishments and Progress

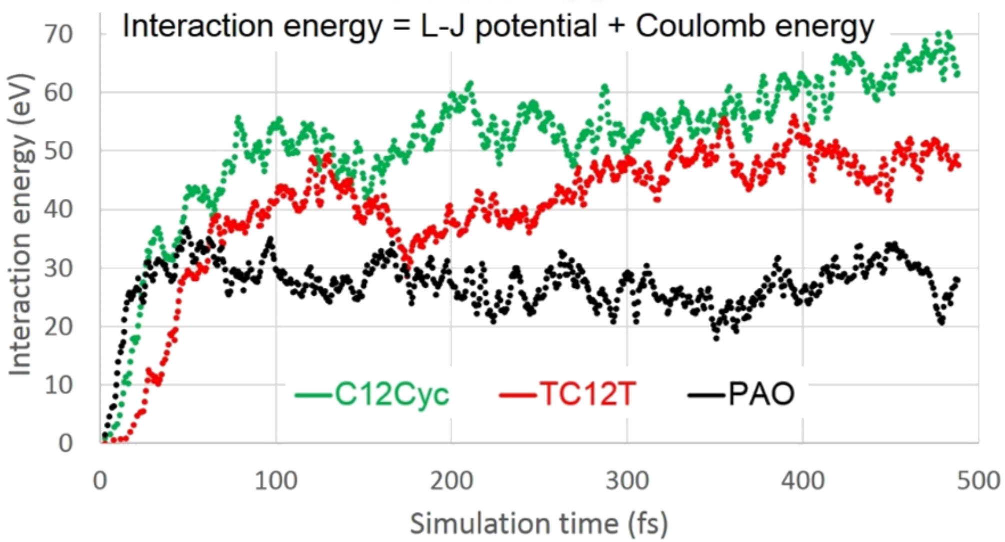
Novel Boundary Lubrication Friction Modifiers: Surface adsorption





Selected MD simulation results are shown here.

As the adsorption takes place, the mass center drops and maintains at a equilibrium position about **10 Å** from the hydrated surface.



The interaction increases during the approaching.

C12Cyc molecules show the highest surface interaction energy.

Such increased interaction energy is well maintained in elevated temperature.

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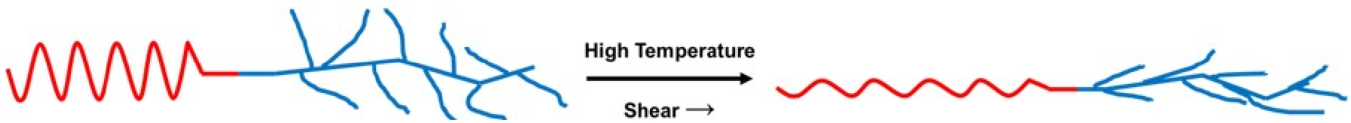
Technical Accomplishments and Progress

Novel Viscosity Modifiers: Synthesis

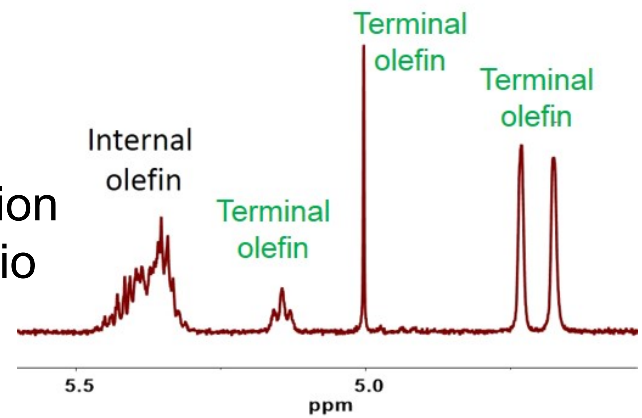
The diblock copolymer is the desired VM.

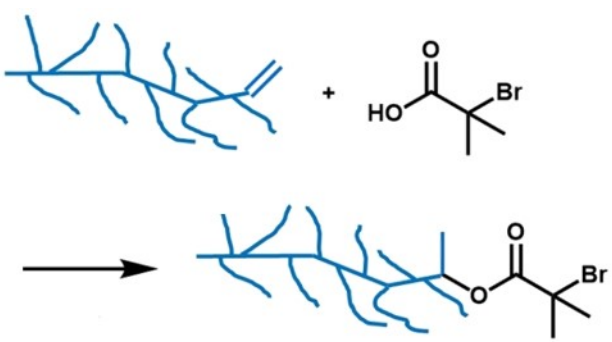


Functionalization of **Vinyl-terminated** polymer chains is **essential** for a successful synthesis!

Addition to the terminal olefin via hydroboration-bromination

Optimized reaction
70 : 30 of **terminal : internal** ratio





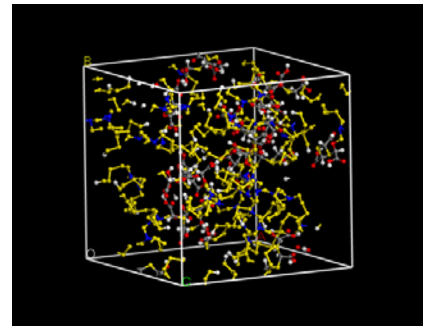
Esterification of vinyl-terminated polymer for final VM synthesis.

GPC Analysis:
Mn = 19K Da; PDI = 2.1

Technical Accomplishments and Progress

Novel Viscosity Modifiers: Shear Thinning Verification

MD system: United atom (UA) model, consider CH_x as a single bead, periodic boundary conditions, 20 molecules.

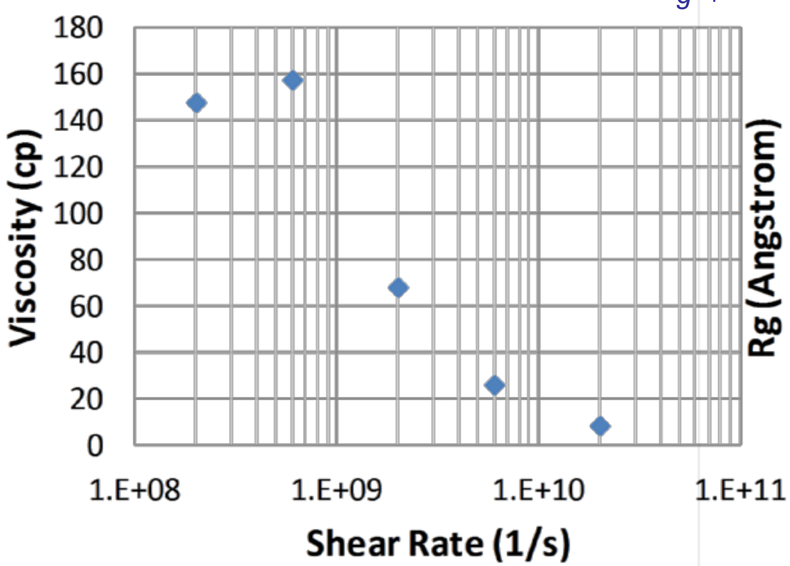


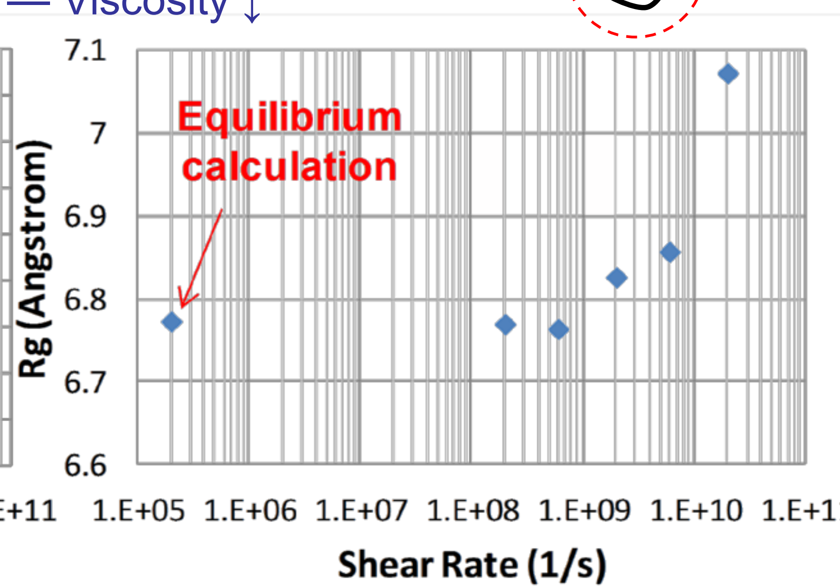
Density: **0.98 g/cm³** (M_n = 1080) at 25 °C, 1 atm

Comparison:

- PAO6 (M_n = 540, ρ = 0.826 g/cm³)
- PAO1000 (Mn = 2930, ρ = 0.851 g/cm³)
- Methyl methacrylate (M_n = 100, ρ = 0.94 g/cm³)
- PMMA (ρ = 1.14-1.2 g/cm³)

$R_g \uparrow$ — Viscosity $\downarrow$

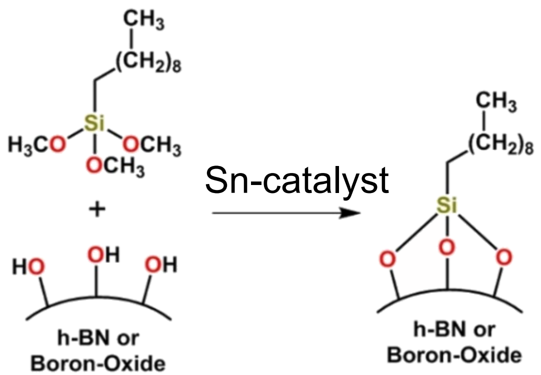




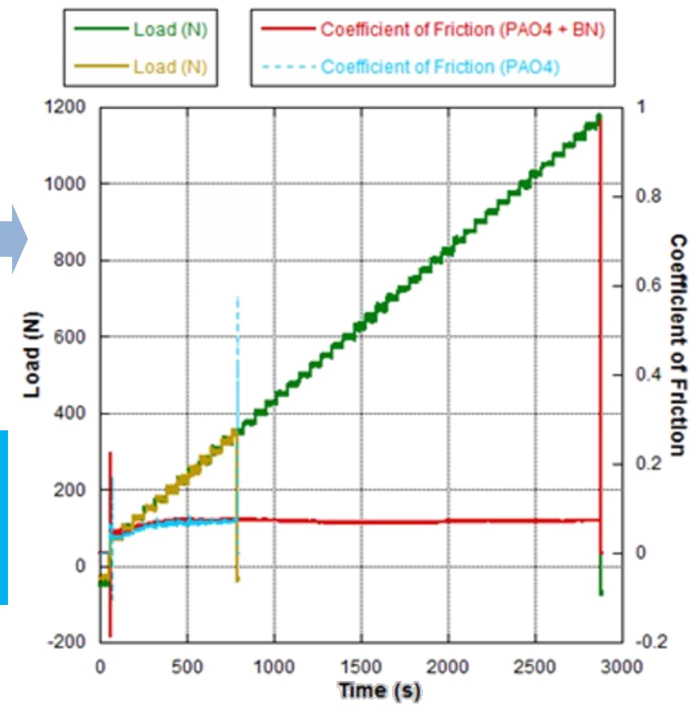
The co-polymer shear thinning is correlated to the change in radius of gyration

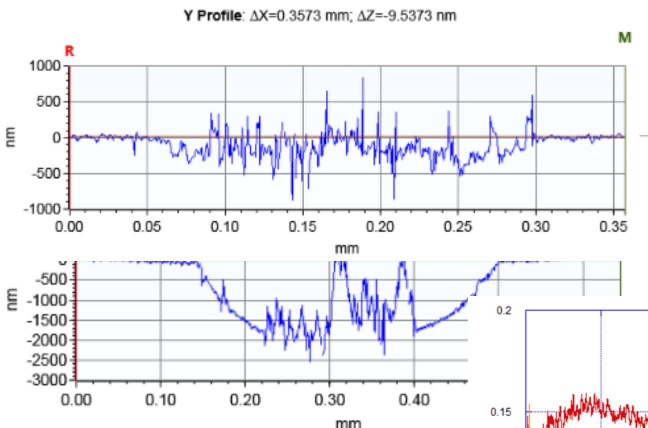
Technical Accomplishments and Progress

Nano Particle Enhancement on Friction and Wear Reduction

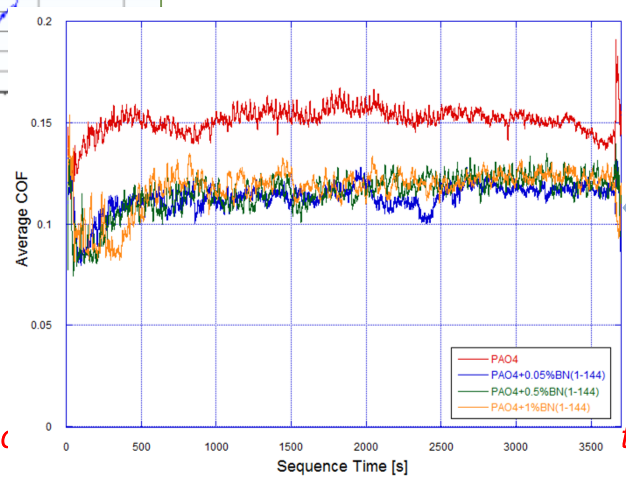


Scuffing resistance is enhanced by more than three times





Wear resistance is enhanced three times

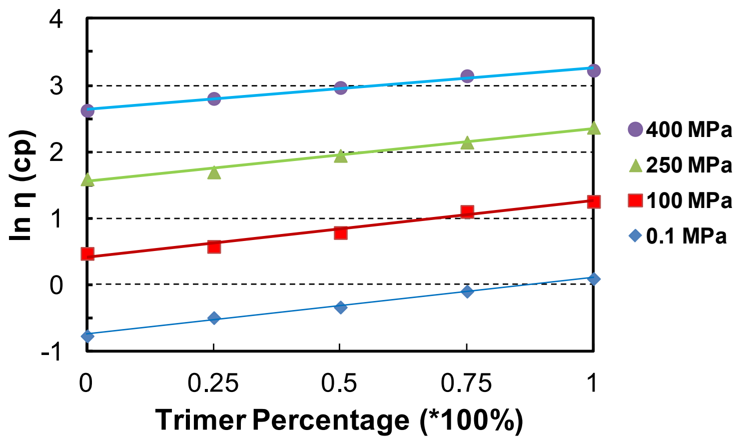


Solubiliy of nanoparticles in the base oil is improved by attaching alkyl chains.

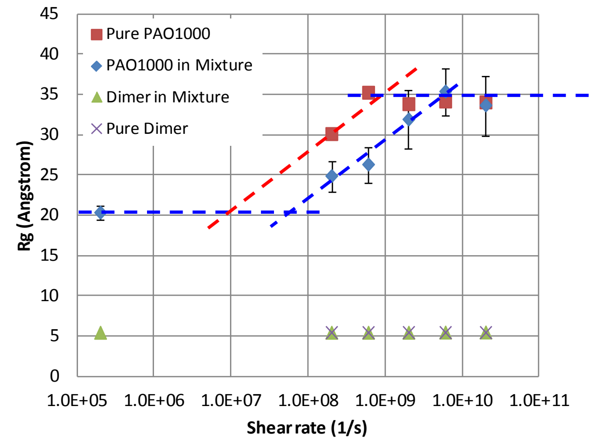
A measurable friction reduction, by more than 20 %, is obtained after the orgnosilane functionalization.

Technical Accomplishments and Progress

Viscosity Modeling: Combined MD Simulations with Empirical Model



MD for base fluid mixture: 1-decene dimer (C_{20}) + 1-decene trimer (C_{30})

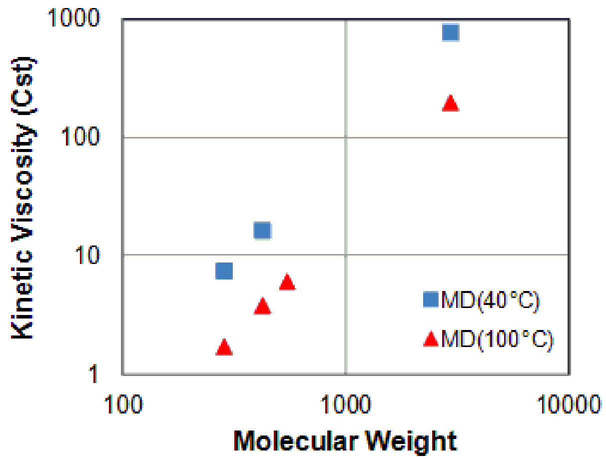


MD for base fluid shear thinning transition

MD + Berry Fox Model for long-chain polymer viscosity

$$F(X) = \left(\frac{N_0}{6}\right) X_c \left(\frac{X}{X_c}\right)^a$$

$$X = Zg(\langle s^2 \rangle_0 / M)\varphi_2 / v_0$$



- Building upon the Berry-Box viscosity model and MD-Based monomer friction calculation, We can model the viscosity of long-chain polymers.
- A novel approach of using radius of gyration for shear-thinning transition is developed.
- Results confirmed by published data.

Responses to previous Year Reviewers' Comments

- **This project is a new start.**

Collaborations

- **Northwestern University and Argonne National Laboratory**
  - Functionalized nanoparticle tribological studies;
  - High temperature high shear (HTHS) experiments, scuffing resistance tests, and tribo-layer measurements;
  - Calculation of friction reduction benefits to the engine system using the Ricardo engine simulation tools.
- **Ashland, Inc.**
  - Supply of base stocks for tribological and rheological tests;
  - Assistance and guidance in lubricant formulation with the newly-synthesized additives;
  - Oxidation stability and shear-viscosity tests.
- **General Motors**:
  - Validation of the test results from NU and ANL;
  - Assistance on the dynamic and thermal effects on lubrication efficiency;
  - Engine tests for fuel consumption and exhaust discharge evaluations.

Remaining Challenges and Barriers

- **Interaction between Additives:** Whether adverse interactions would occur between the newly made or existing additives to be used in an engine oil?
- **Best formulation strategy**: What is the optimal composition of additives for a wide range of temperature and operating conditions for the most friction reduction.
- **Distance between laboratories and industrial applications**: Will the significant friction reduction obtained at lab tests be converted to significant fuel economy improvement?

Future Work

2015

- **Finalize synthesis of the copolymer VM**:
  - Synthesis of diblock Co-polymer: Borane Chain Transfer;
  - Using a chain transfer agent with a suitable catalyst, chain transfer to borane instead of β-H elimination;
- **Further improvement of BL additives**:
  - Mixture or hybrid, optimized terminal groups and chain length.
- **Strategy for further low-friction oils**:
  - Strategy for using heterocyclic FMs, nanoparticles, and copolymer VMs;
  - Lubrication, friction, and rheological properties in wide ranges of temperature and operating conditions, testing and modeling, comparisons with commercial oils.

2016

- Further design improvements of heterocyclic FMs, nanoparticles, and copolymer VMs
- Further laboratory tests at more severe conditions, oil aeration effect.
- Industrial verification tests

Summary

Objective: Novel lubricant formulations for improving vehicle fuel efficiency by at least 2 % without adversely impacting vehicle performance or durability.

Approaches:

- Novel Friction modifiers, viscosity modifiers, functionalized nano Particles.
- Chemical, tribological testing
- Modeling and model-based design

FY 14 Accomplishments

- Three groups of heterocycles friction modifiers have been synthesized, two groups demonstrate a strong friction reduction capability and strong thermal stability even up to 250~300C. The base oil with the heterocycle 2 additives shows a significantly lower friction than a reference fully formulated motor oil does in the boundary lubrication regime (~70% boundary lubrication friction reduction).
- Functionalized nanoparticles show good solubility in the base oil; more than 20% friction reduction and three fold improvements of wear and scuffing resistance have been accomplished.
- A class of novel copolymer viscosity modifier has been designed and initial molecules synthesized.
- A viscosity prediction model has been developed based on MD simulation and the Berry-Box model; a novel approach for shear-thinning transition prediction is identified and verified.

Technical Back-Up Slides

Publications

Conference presentations

- Wang, Q., Junlk, M., Liu,P., Johnson. B., Zolper, T., Marks, T., Chung, Y. W., and Ren, N. and Lockwood, F., “Understanding Lubricant Rheology and Tribology,” Presented at 2014 STLE Annual Meeting, May 2014, Lake Buena Vista, FL, USA.
- Johnson, B., He, H., Jin, D., Liu, J., Desanker, M., Song, C.,, Greco, A., Delferro, M., Erdemir, A., Chung, Y.W., Marks, T. J., and Wang, Q., “Novel Friction Modifiers for Steel Contact,” Presented at the 2014 Tribology Frontiers Conference, Chicago.
- Zolper, T., He. Y, Ren, N, Lockwood, F., Delferro, M., Marks, T., Chung, Y. W., and Wang, Q., “Use of Elastohydrodynamic Film Thickness Measurements to Approximate the Power-Law Exponent and Pressure-Viscosity Index of PAO-OCP Mixtures,” accepted for presentation at the 2015 STLE Annual meeting, May 2015, Dallas, TX, USA.
- Erdemir, A., "Facing the Hard Truth about Friction and Its Impact on Global Energy Consumption," 2014 Distinguished Speaker Series, University of Texas-Arlington, Arlington, TX.

Four Journal papers are under preparation

One invention disclosure is under preparation

Critical Assumptions and Issues

- How to maintain the best behavior of individual additive in a formulated oil?
  - We are further looking for the design of more thermally stable and wider-range applicable friction modifiers through mixing selected best heterocycles, or design and synthesize hybreds.
  - We are testing the new additives in selected base and fully formulated engine oils and investigate the performance of the mixtures and residuals on tested surfaces. The used oils will be tested again for repeatability that should reflect the changes, if any.

- How to ensure long-term friction reduction?
  - In addition to the measures mentioned above, we will also try duration tests under elevated temperature and frequent start-stops.
  - We will work with our industrial partners for more realistic solutions.

- How to compare with commercially mature additives?
  - We will add our new additives to base oils and to formulated oils to conduct comparative studies.
  - We will try to compare the performances of selected individual equivalent additives.